PRODUCTION METHOD OF 4,6-DIAMINORESORCIN

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a novel production method of 4,6-diaminoresorcin which is a monomer for polybenzobisoxazole (PBO). More particularly, it relates to a production method of 4,6-diaminoresorcin in which resorcin is used as a starting material, any step of forming a halogen-containing compound is not required and the production of by-products is inhibited. Furthermore, the present invention relates also to a novel intermediate useful for the synthesis of 4,6-diaminoresorcin and a production method of this intermediate.

A PBO fiber is superior to conventional fibers in terms of various properties such as strength, modulus of elasticity, heat resistance and chemical resistance, as disclosed in Japanese Patent Publication No. 501452/1986, so that it is expected to apply this kind of fiber to various uses including structural materials and thermal insulating materials as a super fiber which is superior to aramid, and hence the fiber is considered to be an industrially extremely useful resin. 4,6-Diaminoresorcin is a monomer for the PBO, and therefore, it is important as a raw material for the PBO.

2. Description of the Related Art

A PBO is a polymer represented by the following general structural formula (c) and can be obtained through a condensation reaction between a compound (a) and a compound (b) as represented by the following reaction formula:

(a)   (b)   (c)
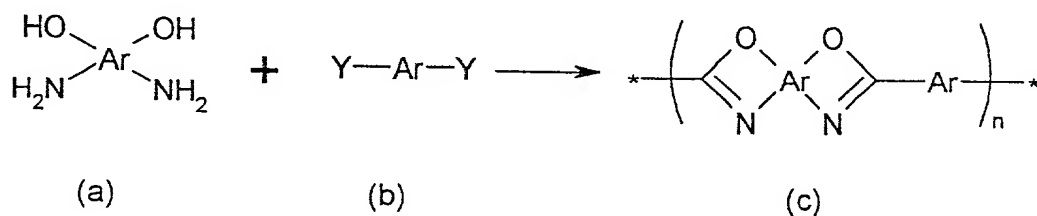
wherein Ar is an aromatic group; and Y is a functional group having an electron-deficient carbon such as a carboxyl group, a carboxylic acid halide group, a haloalkyl group or a nitrile group.

The thus obtained polybenzobisoxazole is used as fibers, films and the like, but its physical properties such as strength and modulus of elasticity are greatly influenced by a polymerization degree of the polymer. It is known that in a polycondensation reaction, a maximum polymer viscosity is generally obtained when a feed ratio of the monomers is 1:1, and the polymer viscosity rapidly decreases as the feed ratio of the monomers deviates from a ratio of 1:1. That is, to attain a satisfactory sufficient polymerization degree, it is necessary to strictly control the feed ratio of the monomers.

However, in the case that the monomers contain impurities in large quantities, it is difficult to control this feed ratio of the monomers. Particularly, when the

monomers contain even small amounts of monoamine and triamines which act as polymerization terminators, the deterioration of the polymerization degree is caused. Therefore, there have been desired the high-purity monomers containing neither the monoamine nor the triamines.

As a monomer (a) for the PBO, 4,6-diaminoresorcin is known, and several synthesis methods for this compound have been reported.

A conventional production method of 4,6-diaminoresorcin comprises synthesizing dinitroresorcin as a precursor by a method in which resorcin is acetylated and then nitrated (Ber. Dtsch. Chem. Ges., 16, 552, 1883), a method in which 1,3-bis(alkyl carbonate)benzene is nitrated (Japanese Patent Application Laid-Open No. 136/1990) or another method, and then reducing the thus synthesized dinitroresorcin.

However, the operation of this conventional method is complicated and a manufacturing cost increases, because protecting groups are introduced for the hydroxy groups of resorcin, and from an industrial viewpoint, the above method has a problem that the protecting groups eliminated in a hydrolysis step become an unrecoverable by-product, and a problem that a trinitro compound is produced in the nitration step and a triamino compound is produced in the reduction step, and they disturb the polymerization in the synthesis of the PBO.

Furthermore, several methods using no protecting groups have been proposed in which a halobenzene is used as a raw material, and there are known, for example, a method in which a trichlorobenzene is nitrated (Japanese Patent Application Laid-Open No. 500743/1990) and a method in which a dihalobenzene is nitrated and then hydrolyzed with an alkali (Japanese Patent Application Laid-Open Nos. 238561/1989, 233127/1995, 316102/1995 and 73417/1996).

In these methods, however, since 4,6-dinitro-resorcin is unstable under the alkali conditions in the hydrolysis step, the operation of these methods is apt to be complicated in order to avoid the decomposition of produced 4,6-dinitroresorcin. Furthermore, trichlorobenzene and its nitrated compound have a problem that they are strongly poisonous and cause an irritation on skin. Therefore, it is not preferable in consideration of the safety of an operator to pass through the production of a halogen-containing compound such as the halobenzene and its nitrated compound.

In addition, another method which comprises subjecting an aniline to diazotization and diazo-coupling the thus diazotized compound to resorcin, followed by hydrocracking is disclosed in Japanese Patent Application Laid-Open Nos. 242604/1995 and 124575/1997. In this method, however, aniline produced by the hydrocracking might be mixed with the product, and might disturb the polymeriza-

tion in the synthesis of the PBO.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel production method of 4,6-diaminoresorcin in which any step of forming a halogen-containing compound is not required and the production of by-products is inhibited.

It is another object of the present invention to provide a production method of 4,6-dinitroresorcin, as a precursor of 4,6-diaminoresorcin, via the production of a novel intermediate.

It is still another object of the present invention to provide a production method of a high-molecular-weight PBO by the use of high-purity 4,6-diaminoresorcin obtained by these methods.

The present inventors have made intensive studies to solve the above problems, and found that 4,6-diaminoresorcin can be obtained at a high yield by sulfonating resorcin to form resorcin 2,4,6-trisulfonate, nitrating resorcin 2,4,6-trisulfonate to obtain 2-sulfonic acid-4,6-dinitroresorcin with a high position selectivity, hydrolyzing this compound to form 4,6-dinitroresorcin, and then reducing the same. In consequence, the present invention has been attained.

Furthermore, the present inventors have found that a high-molecular-weight PBO can be obtained by hydrolyzing

2-sulfonic acid-4,6-dinitroresorcin to obtain 4,6-
dinitroresorcin containing neither isomers nor trinitro
compounds, reducing this compound to obtain high-purity
4,6-diaminoresorcin, and then polymerizing the same. Thus,

5   the present invention has been achieved.

That is, the present invention includes the fol-
lowing aspects.

1.   A production method of resorcin 2,4,6-
trisulfonate which comprises the step of bringing resorcin

10   into contact with a sulfonating agent.

2.   The production method of resorcin 2,4,6-
trisulfonate according to the above (1), wherein fuming
sulfuric acid is used as the sulfonating agent.

3.   The production method of resorcin 2,4,6-

15   trisulfonate according to the above (2), wherein fuming
sulfuric acid to be used contains 3 mols or more of free
SO_3 per mol of resorcin.

4.   A production method of 2-sulfonic acid-4,6-
dinitroresorcin which comprises the step of nitrating re-

20   sorcin 2,4,6-trisulfonate.

5.   The production method of 2-sulfonic acid-4,6-
dinitroresorcin according to the above (4), wherein the ni-
tration is carried out in sulfuric acid or a fuming sulfu-
ric acid solvent.

25   6.   A production method of 2-sulfonic acid-4,6-
dinitroresorcin which comprises the following steps:

(1) a first step of producing resorcin 2,4,6-trisulfonate by bringing resorcin into contact with a sulfonating agent, and

(2) a second step of producing 2-sulfonic acid-4,6-dinitroresorcin by bringing resorcin 2,4,6-trisulfonate into contact with a nitrating agent.

7.   A production method of 4,6-dinitroresorcin which comprises the step of hydrolyzing 2-sulfonic acid-4,6-dinitroresorcin.

8.   The production method of 4,6-dinitroresorcin according to the above (7), wherein the hydrolysis is carried out in water or an aqueous mineral acid solution.

9.   The production method of 4,6-dinitroresorcin according to the above (8), wherein sulfuric acid is used as the mineral acid.

10.   A production method of 4,6-dinitroresorcin which comprises the following steps:

(1) a first step of producing resorcin 2,4,6-trisulfonate by bringing resorcin into contact with a sulfonating agent,

(2) a second step of producing 2-sulfonic acid-4,6-dinitroresorcin by bringing resorcin 2,4,6-trisulfonate into contact with a nitrating agent, and

(3) a third step of producing 4,6-dinitroresorcin by hydrolyzing 2-sulfonic acid-4,6-dinitroresorcin.

11.   A production method of 4,6-diaminoresorcin

which comprises the following steps:

(1) a first step of producing resorcin 2,4,6-trisulfonate by bringing resorcin into contact with a sulfonating agent,
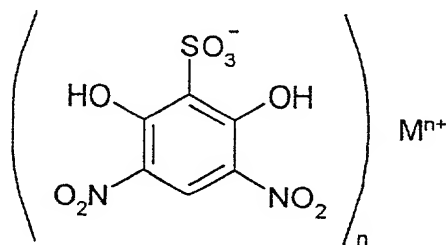
(2) a second step of producing 2-sulfonic acid-4,6-dinitroresorcin by bringing resorcin 2,4,6-trisulfonate into contact with a nitrating agent,

(3) a third step of producing 4,6-dinitroresorcin by hydrolyzing 2-sulfonic acid-4,6-dinitroresorcin, and

(4) a fourth step of producing 4,6-diaminoresorcin by reducing 4,6-dinitroresorcin.

12. A production method of polybenzobisoxazole which comprises the steps of hydrolyzing 2-sulfonic acid-4,6-dinitroresorcin, followed by reducing to obtain 4,6-diaminoresorcin, and then reacting the thus obtained 4,6-diaminoresorcin with aromatic dicarboxylic acid.

13. 2-Sulfonic acid-4,6-dinitroresorcin represented by the following formula and salts thereof:

$$\left(\begin{array}{c} \text{HO} \overset{\displaystyle SO_3^-}{\underset{O_2N \qquad NO_2}{\bigcirc}} \text{OH} \end{array} \right)_n M^{n+}$$

wherein M is hydrogen, an alkali metal or an alkaline earth metal, and n is 1 or 2.

14. A production method of 4,6-diaminoresorcin which comprises:

(1) a first step of producing 4,6-dinitroresorcin by hydrolyzing 2-sulfonic acid-4,6-dinitroresorcin, and

5   (2) a second step of producing 4,6-diaminoresorcin by reducing 4,6-dinitroresorcin.

15. The production method of 4,6-diaminoresorcin according to the above (14), wherein 2-sulfonic acid-4,6-dinitroresorcin is obtained by the following steps:

10   (1) a first step of producing resorcin 2,4,6-trisulfonate by bringing resorcin into contact with a sulfonating agent, and

(2) a second step of producing 2-sulfonic acid-4,6-dinitroresorcin by bringing resorcin 2,4,6-trisulfonate

15 into contact with a nitrating agent.

16. The production method of 4,6-diaminoresorcin according to the above (14), wherein in the second step, 4,6-dinitroresorcin is reduced in an aqueous mineral acid solution.

20   17. The production method of 4,6-diaminoresorcin according to the above (16), wherein hydrochloric acid is used as the mineral acid.

18. The production method of 4,6-diaminoresorcin according to the above (14) which comprises the steps of

25 dissolving or suspending 4,6-dinitroresorcin in a solvent, adjusting the pH of the suspension in a range of 4 to 5 to

obtain 4,6-dinitroresorcin, and then reducing the thus ob-
tained 4,6-dinitroresorcin.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A production method of 4,6-diaminoresorcin of the
present invention can be accomplished via the following in-
termediate compounds.
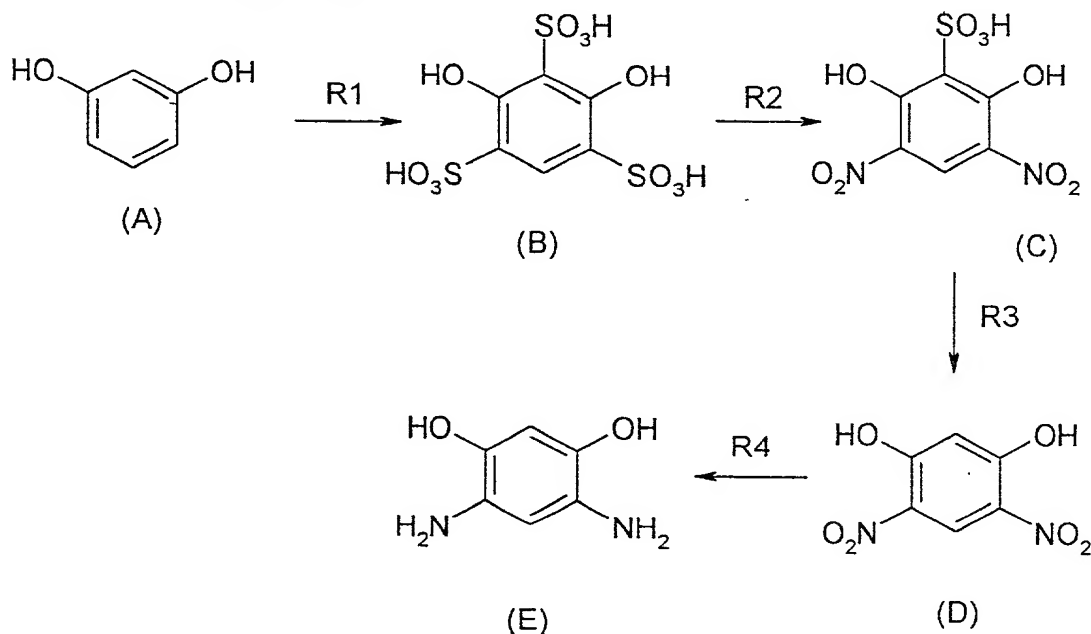
First, resorcin (i.e., 1,3-benzenediol) (A) as a
raw material is brought into contact with a sulfonating
agent (reaction R1) to obtain resorcin 2,4,6-trisulfonate
(B). Successively, sulfonic groups at positions 4 and 6
are selectively nitrated (reaction R2) to obtain 2-sulfonic
acid-4,6-dinitroresorcin (C), which is then hydrolyzed (re-
action R3) to obtain 4,6-dinitroresorcin (D). Finally,
4,6-dinitroresorcin (D) is reduced (reaction R4) to obtain
desired 4,6-diaminoresorcin (E).

To produce resorcin 2,4,6-trisulfonate, as de-
scribed in Berichite, 10, 182, there is known a method in
which a disulfonic acid resorcin is heated at 200°C in fum-
ing sulfuric acid. However, in the case that the thus

5 formed disulfonic acid resorcin is isolated and then used
in the subsequent step, a process becomes complicated and
the serious decrease of yield occurs. Thus, the above
method has been unsuitable for industrial practice.

Next, each of the reaction steps R1 to R4 will be

10 described in detail hereinafter.

In the first reaction step R1, a sulfonating agent
can be used that sulfonates resorcin (A) to produce resor-
cin 2,4,6-trisulfonate (B). Illustrative examples of the
sulfonating agent include concentrated sulfuric acid, fum-

15 -ing sulfuric acid and sulfur trioxide. The reaction may be
carried out using an appropriate solvent. However, it is
industrially advantageous that the reaction is carried out
in excess concentrated sulfuric acid or fuming sulfuric
acid without using a solvent. To avoid desulfonation

20 caused by hydrolysis, concentrated sulfuric acid or fuming
sulfuric acid is preferably used at a concentration of 80
to 100% by weight, more preferably 95% by weight or more.
Above all, the use of fuming sulfuric acid is most prefer-
able.

25 According to the investigation of the present in-
ventors, the selectivity of resorcin 2,4,6-trisulfonate de-

pends largely on the concentration of SO_3 in sulfuric acid.
As the SO_3 concentration in sulfuric acid decreases, the
selectivity of resorcin 2,4,6-trisulfonate decreases. For
example, even if 95 wt% sulfuric acid (SO_3 concentration =
5   77.6%) is used, the preparation of resorcin 2,4,6-
trisulfonate is possible, but it has been confirmed that in
the case that 95 wt% sulfuric acid (SO_3 concentration =
77.6%) is used, the selectivity of resorcin 2,4,6-
trisulfonate is in a range of about 12 to 17 mol%, and re-
10 maining 83 to 88 mol% thereof is resorcin 4,6-disulfonate.
This fact can be considered to be due to the decrease of
the sulfuric acid concentration by water produced during
the reaction. To attain such a yield as can be industri-
ally satisfied, it is desirable that the SO_3 concentration
15 in sulfuric acid at the completion of the reaction is 81.6%
or more, i.e., the sulfuric acid concentration is about
100% or sulfuric acid contains an excessive amount of free
SO_3. To maintain such a state, the sulfonation should be
carried out by using fuming sulfuric acid containing 3 mols
20 or more of free SO_3 per mol of resorcin.

The amount of the sulfonating agent to be used is
not particularly limited, as long as it satisfies the above
SO_3 concentration. It is, however, preferably 5 to 50
times more by weight than resorcin in view of volumetric
25 efficiency and efficient agitation.

To bring resorcin into contact with the sulfonat-

ing agent, one of them may be added to the other or vice versa.

As for a reaction temperature, the reaction may be carried out within any temperature range in which the desired product can be obtained. However, a temperature range of from about 0 to about 200°C is preferable. To avoid the installation of large cooling facilities which is required for heat generation at the time of the sulfonation, the reaction temperature is desirably 20°C or higher. To prevent an undesirable side reaction, the reaction temperature is desirably 150°C or lower.

Resorcin 2,4,6-trisulfonate can be isolated from a reaction mass by adding dropwise the reaction mass to an aqueous solution of an inorganic salt such as sodium sulfate to cause salting-out, followed by filtering and drying.

Next, reference will be made to the reaction step R2 in which 2-sulfonic acid-4,6-dinitroresorcin (C) is obtained from resorcin 2,4,6-trisulfonate (B). The reaction step R2 is a nitration step, in which a known nitrating agent capable of producing the desired compound can be used. Illustrative examples of the nitrating agent include nitric acid, fuming nitric acid, and nitrates such as sodium nitrate and potassium nitrate. The nitration may be carried out after the isolation of resorcin 2,4,6-trisulfonate from the sulfonated reaction mass as described above, but it is industrially advantageous that the nitration is carried out

in a one-pot manner by adding the nitrating agent to the
sulfonated reaction mass (in this case, the nitration is
carried out in sulfuric acid or a fuming sulfuric acid sol-
vent). The amount of the nitrating agent to be used is in

5   a range of about 1 to 10 mols per mol of resorcin (A) as a
starting material, and in order to sufficiently promote the
reaction and to inhibit the excessive nitration, it is
preferably in a range of about 2 to 4 mols per mol of re-
sorcin (A).

10   The reaction step R2 can also be carried out
within any temperature range in which the desired product
can be obtained. However, when the reaction temperature is
too high, the reaction proceeds quickly, whereby the unde-
sirable side reaction may occur on occasion. Therefore,

15   the reaction is usually carried out while the reaction tem-
perature is controlled by cooling. The reaction tempera-
ture is preferably in a range of about 0 to 80°C, more
preferably about 0 to 50°C.

To isolate desired 2-sulfonic acid-4,6-

20   dinitroresorcin (C) from the reaction mass after the com-
pletion of the reaction, the reaction mass is first neu-
tralized with an alkali to form an alkali metal salt or an
alkaline earth metal salt, which is then subjected to salt-
ing-out to thereby deposit the salt, so that the desired

25   salt is obtained as a mixture with an alkali metal salt or
an alkaline earth metal salt of sulfuric acid. In succes-

sion, the mixture is added to, for example, a mixed soluti-
on containing water and ethanol in a ratio of 2:8, and the
resultant solution is then heated at 50 to 80°C to dissolve
the desired compound. Afterward, the inorganic salt is re-
moved by filtration under heating. The resultant filtrate
is cooled to deposit yellow crystals, which are then fil-
tered to thereby obtain an alkali metal salt or an alkaline
earth metal salt of 2-sulfonic acid-4,6-dinitroresorcin (C).
Alternatively, the solvent may be removed from the filtrate
to obtain the alkali metal salt or the alkaline earth metal
salt of 2-sulfonic acid-4,6-dinitroresorcin (C). The alka-
li metal salt or the alkaline earth metal salt can be de-
salted by dissolving the salt in water, passing the solu-
tion through a column filled with a strongly acidic cation
exchange resin, and removing water therefrom. In conse-
quence, 2-sulfonic acid-4,6-dinitroresorcin (C) is obtained.

Next, reference will be made to the reaction step
R3 in which 2-sulfonic acid-4,6-dinitroresorcin (C) is hy-
drolyzed to obtain 4,6-dinitroresorcin (D).

The hydrolysis is carried out in water or an aque-
ous solution containing an acid or an alkali as a catalyst.
However, it is preferably carried out in water or the acid-
containing aqueous solution, more preferably in a mineral
acid-containing aqueous solution, because there is a fear
that 4,6-dinitroresorcin (D) after the hydrolysis may bring
about a further decomposition reaction in the alkali aque-

ous solution having a high concentration. Examples of the
mineral acid which can be used herein include sulfuric acid,
hydrochloric acid and phosphoric acid. The mineral acid is
preferably sufficiently diluted with water, or a sulfuric

5 acid coupling agent may be added thereto in order to avoid
the recombination of the separated sulfonic group. In the
hydrolysis step R3, the concentration of the mineral acid
is preferably in a range of 5 to 90% by weight, and in or-
der to maintain a sufficient hydrolysis rate and to obtain

10 a sufficient yield, it is desirably 10% by weight or more.
The amount of the aqueous mineral acid solution to be used
is not particularly limited, but it is preferably about 2
to 50 times by weight more than 2-sulfonic acid-4,6-
dinitroresorcin (C) in view of agitation efficiency and

15 volumetric efficiency. The reaction temperature is prefer-
ably in a range of from 50°C to reflux temperature or so.

This hydrolysis step R3 may be carried out after
2-sulfonic acid-4,6-dinitroresorcin (C) has been isolated,
or alternatively it may be carried out without isolating 2-

20 sulfonic acid-4,6-dinitroresorcin (C) from the reaction
mass in the nitration step R2.

When the hydrolysis is directly carried out
without isolating 2-sulfonic acid-4,6-dinitroresorcin (C),
the reaction mass in the nitration step R2 is diluted so as

25 to become the aqueous mineral acid solution which meets
predetermined conditions. Furthermore, when 2-sulfonic

acid-4,6-dinitroresorcin is isolated as the alkali metal salt or the alkaline earth metal salt, the salt may be directly used as it is in the hydrolysis step. In addition, the salt may be used in the form of a mixture with an al-

5 kali sulfate.

As the hydrolysis reaction proceeds, crystals of 4,6-dinitroresorcin (D) are gradually deposited. Therefore, these crystals are filtered after the completion of the reaction to-obtain the desired product. The thus obtained

10 4,6-dinitroresorcin (D) may be purified as required prior to its use. The compound 4,6-dinitroresorcin (D) may be purified by subjecting it to sludging in or recrystallization from a solvent such as ethanol. However, it is preferable for the purpose of preventing the deterioration of a

15 catalytic activity in the reduction step to dissolve or suspend 4,6-dinitroresorcin (D) in a solvent such that the resulting solution has a pH of 4 to 5. Concretely, any of the following procedures can be taken.

(1) An alkali is added to a solution or slurry in

20 which 4,6-dinitroresorcin is dissolved or suspended in a solvent, thereby adjusting the pH in a range of 4 to 5.

(2) 4,6-Dinitroresorcin is dissolved in a two-layer mixed solvent of water and a hydrophobic solvent, and an alkali is then added to the solution, thereby adjusting

25 the pH in a range of 4 to 5.

(3) 4,6-Dinitroresorcin, which is in the form of

an alkali salt, is dissolved in water, and an acid is then
added to the solution, thereby adjusting the pH in a range
of 4 to 5.

Examples of a hydrophilic solvent which is one ty-
5 pe of the solvent to be used include water, methanol, etha-
nol, n-propanol, iso-propanol, DMI (1,3-dimethyl-2-
imidazolidinone) and DMF (N,N-dimethylformamide). Examples
of a hydrophobic solvent which is the other type of the
solvent to be used include ethyl acetate, 1,3-
10 dimethoxybenzene, phenetole and anisole. The amount of the
solvent depends on the kind of solvent to be used, but it
is in a range of 1 to 100 times more than that of 4,6-
dinitroresorcin. The above alkali is not particularly lim-
ited, but its examples include potassium hydroxide, sodium
15 hydroxide, potassium carbonate and sodium carbonate. The
above acid is not particularly limited, but its examples
include mineral acid such as hydrochloric acid and sulfuric
acid. A temperature at the pH adjustment depends on the
kind of solvent to be used, but it is preferably in a range
20 of 10 to 80°C.

The isolation of purified 4,6-dinitroresorcin, in
the case that the pH adjustment is made in the slurry state,
is carried out by filtrating the slurry as it is, washing
the collected substance with the used solvent, and further
25 washing it with water. In the case that the pH adjustment
is made in the two-layer heterogeneous state, the isolation

is carried out by allowing the obtained solution to stand

for separation, washing the separated organic phase with

water, cooling it for crystallization, and then filtering

the resultant crystals. In the case that 4,6-

5   Dinitroresorcin in the form of the alkali salt is dissolved

and the acid is then added, the isolation is carried merely

by filtrating the obtained mixture as it is, and then wash-

ing it with water.

Finally, reference will be made to the reduction

10   step R4 in which 4,6-diaminoresorcin (E) is obtained from

4,6-dinitroresorcin (D).

In this step, any reduction technique may be used

as long as the desired product is obtained. However, a

catalytic reduction is usually carried out in the presence

15   of a noble metal catalyst. The noble metal catalyst to be

used herein is a platinum group metal such as palladium,

platinum, rhodium or ruthenium which is carried on a proper

carrier, and it is preferable to use palladium or platinum

carried on carbon.

20   The amount of the catalyst to be used is in a

range of 0.1 to 10% by weight, preferably 0.5 to 5% by

weight, based on 4,6-dinitroresorcin (D). A reaction tem-

perature is in a range of 20 to 100°C, and a hydrogen pres-

sure is in a range of 0.1 to 10 MPa.

25   The solvent usable in the reaction is water, an

organic solvent, an organic acid, or a mixture of water and

a mineral acid. Examples of the usable mineral acid in-
clude hydrochloric acid, phosphoric acid and sulfuric acid.
Above all, the employment of hydrochloric acid is prefer-
able, because a hydrochloride of 4,6-diaminoresorcin is

5 formed simultaneously with the reduction of 4,6-
dinitroresorcin and this hydrochloride is dissolved in wa-
ter to form a homogeneous solution which is easy to handle.
Examples of the organic solvent include aromatic hydrocar-
bons such as benzene and toluene, and alcohols such as

10 methanol and ethanol. Examples of the organic acid include
acetic acid and propionic acid.

The formed 4,6-diaminoresorcin (E) is converted
into a mineral acid salt to avoid oxidation/decomposition,
and this salt is then isolated by a known technique such as

15 precipitation or filtration. More specifically, for exam-
ple, the reaction mass is added to a diluted aqueous hydro-
chloric acid solution containing stannous chloride to dis-
solve 4,6-diaminoresorcin hydrochloride. In succession,
the resulting solution is filtered to remove the catalyst,

20 and then the solvent is distilled off under reduced pres-
sure. Alternatively, the filtrated solution is mixed with
concentrated hydrochloric acid to deposit crystals, fol-
lowed by filtration. When the aqueous hydrochloric acid
solution is used as the solvent, 4,6-diaminoresorcin hydro-

25 chloride is already formed in the reduction reaction mass,
and hence the steps of the salt-forming and the dissolving

are not necessary. When phosphoric acid or sulfuric acid
is used as the mineral acid and the 4,6-diaminoresorcin
mineral acid salt is deposited, the salt is dissolved in
the form of 4,6-diaminoresorcin hydrochloride by salt-
exchanging, and crystals are then deposited in the similar
manner as above.

An obtained 4,6-diaminoresorcin dimineral acid
salt can be further purified by a technique such as recrys-
tallization. Concretely, for example, after crude 4,6-
diaminoresorcin dimineral acid salt is dissolved in water
including stannous chloride, activated carbon is added
thereto, followed by treatment. Next, the activated carbon
is removed by filtration, and concentrated hydrochloric
acid is then added thereto for crystallization.

In order to obtain a PBO by the use of the thus
obtained 4,6-diaminoresorcin (E), a known polymerization
method can be employed. For example, the PBO can be ob-
tained by dissolving the 4,6-diaminoresorcin dimineral acid
salt in polyphosphoric acid, heating the resulting solution
under reduced pressure to remove hydrochloric acid, adding
a required amount of diphosphorus pentoxide, further adding
aromatic dicarboxylic acid in a nearly equimolar amount to
4,6-diaminoresorcin, and then stirring the mixture under
heat. Examples of the usable aromatic dicarboxylic acid
include terephthalic acid, isophthalic acid, 4,4'-
bis(benzoic acid), 4,4'-oxybis(benzoic acid) and 2,6-

naphthalene dicarboxylic acid.

The present invention will be described in more detail with reference to the following examples, by which the present invention is not limited.

5   Example 1 (Sulfonation step R1)

100 g of 30 wt% fuming sulfuric acid (SO_3 concentration = 87.1%, the amount of free SO_3 = 3.75 mols per mol of resorcin) were cooled with ice, 11.0 g (0.1 mol) of resorcin were slowly added thereto. Afterward, the mixture

10   was heated to 90°C to give a dark-red homogeneous solution of a reaction mass. According to the analysis of liquid chromatography (hereinafter abbreviated to "HPLC"), any peaks of resorcin and resorcin 4,6-disulfonate were not confirmed, and the production ratio of resorcin 2,4,6-

15   trisulfonate was 99.8 mol%.

Conditions for HPLC analysis

Column: YMC-312A (ODS)

Mobile phase: Acetonitrile:water:PIC = 1000:2000:10

PIC = Tetrabutyl ammonium hydroxide

20   Flow rate: 1 ml/min

Detection wavelength: 254 nm

Thermostat layer: 40°C

Example 2 (Sulfonation step R1)

100 g of 24 wt% fuming sulfuric acid (SO_3 concentration

25   tration = 86.0%, the amount of free SO_3 = 3 mols per mol of resorcin) were cooled with ice, and 11.0 g (0.1 mol) of re-

sorcin were slowly added thereto. Afterward, the mixture was heated to 50°C to give a dark-red homogeneous solution of a reaction mass. According to the analysis of HPLC, the production ratio of resorcin 4,6-disulfonate was 0.6 mol%,

5 and that of resorcin 2,4,6-trisulfonate was 99.3 mol%.

Example 3 (Sulfonation step R1)

100 g of 16 wt% fuming sulfuric acid (SO_3 concentration = 84.6%, the amount of free SO_3 = 2 mols per mol of resorcin) were cooled with ice, and 11.0 g (0.1 mol) of re-

10 sorcin were slowly added thereto. Afterward, the mixture was heated to 90°C, so that a reaction mass was obtained in the state of an orange-colored viscous slurry containing a slight amount of a solid. According to the analysis of HPLC, the production ratio of resorcin 4,6-disulfonate was

15 9.5 mol%, and that of resorcin 2,4,6-trisulfonate was 90.2 mol%. The reaction mass was further heated to 130°C to obtain a red homogeneous solution, but after reaction for 30 minutes, the production ratio of resorcin 4,6-disulfonate was 13 mol%, and that of resorcin 2,4,6-trisulfonate was 87

20 mol%.

Example 4 (Sulfonation step R1)

100 g of 100 wt% sulfuric acid (SO_3 concentration = 81.6%) were cooled with ice, and 11.0 g (0.1 mol) of resor-cin were slowly added thereto. Afterward, the mixture was

25 heated to 90°C, so that a reaction mass was obtained in the state of a light pink slurry. According to the analysis of

HPLC, the production ratio of resorcin 4,6-disulfonate was 93 mol%, and that of resorcin 2,4,6-trisulfonate was 6.5 mol%. The reaction mass was further heated to 130°C, but no dissolution of crystals was observed, and the reaction mass remained in the form of the light pink slurry. After reaction for 60 minutes, the production ratio of resorcin 4,6-disulfonate was 79 mol%, and that of resorcin 2,4,6-trisulfonate was 21 mol%.

Example 5 (Sulfonation step R1)

100 g of 95 wt% sulfuric acid (SO_3 concentration = 77.6%) were cooled with ice, and 11.0 g (0.1 mol) of resorcin was slowly added thereto. Afterward, the mixture was heated to 50°C, so that a reaction mass was obtained in the state of a white slurry. According to the analysis of HPLC, the production ratio of resorcin 4,6-disulfonate was 88 mol%, and that of resorcin 2,4,6-trisulfonate was 12 mol%.

Example 6 (sulfonation step R1)

200 g of 95 wt% sulfuric acid (SO_3 concentration = 77.6%) were cooled with ice, and 11.0 g (0.1 mol) of resorcin was slowly added thereto. Afterward, the mixture was heated to 50°C, so that a reaction mass was obtained in the state of a white slurry. According to the analysis of HPLC, the production ratio of resorcin 4,6-disulfonate was 83 mol%, and that of resorcin 2,4,6-trisulfonate was 17 mol%.

Example 7 (Nitration step R2)

In the same manner as in Example 1, 5.5 g (0.05

mol) of resorcin were added to 50 g of 30 wt% fuming sulfu-
ric acid, and the resultant sulfonated mass was then cooled
with ice. Afterward, 10.5 g (0.1 mol) of 60 wt% nitric
acid were added dropwise thereto, so that heat was vigor-

5   ously generated and the reaction mass became a yellow-brown
slurry.

This nitrated mass was added to 100 g of ice, and
27.7 g of a 49% aqueous sodium hydroxide solution were then
added dropwise thereto under ice cooling, so that yellow-

10 white crystals were deposited to form a slurry. The slurry
was filtered, and the resultant filter cake was then washed
with 100 g of ethanol to obtain 9.44 g of a mixture of 2-
sulfonic acid-4,6-dinitroresorcin sodium salt and sodium
sulfate.

15   5.04 g of the above mixture were added to 200 g of
a mixed solution of water and ethanol in a ratio of 20:80.
After the mixture was sludged and filtered under heat at
80°C, the filtrate was cooled by allowing it to stand at
room temperature, so that the deposition of crystals was

20 observed. Next, the crystals were collected by filtration
to obtain 1.07 g of yellow crystals of 2-sulfonic acid-4,6-
dinitroresorcin sodium salt.

1.07 g of this compound were dissolved in 25 g of
water, and the resultant solution was passed through a co-

25 lumn filled with 20 ml of an ion exchange resin (MD-S1368)
and then washed with 30 g of water. This solution was

evaporated by an evaporator, dried under nitrogen, washed with ethanol, and then filtered to obtain 130 mg of crystals of 2-sulfonic acid-4,6-dinitroresorcin.

The ^{13}C-NMR spectrum of 2-sulfonic acid-4,6-dinitroresorcin synthesized in this example showed the following absorptions, and these absorptions were ascribed to carbons a to d in the following structural formula, respectively.

δ = 119.4 ppm   a (aromatic carbon substituted by NO_2)

δ = 125.2 ppm   b (aromatic carbon substituted by SO_3H)

δ = 128.9 ppm   c (aromatic carbon to which hydrogen was
        bonded)

δ = 155.0 ppm   d (aromatic carbon substituted by OH)
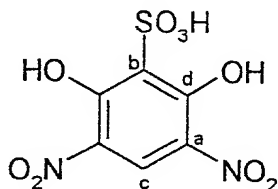
Furthermore, according to the measurement of an infrared-absorbing spectrum, the following distinctive absorption bands were observed.

1588 cm^{-1} NO_2 (absorbing band due to asymmetric stretching
        vibration)

1363 cm^{-1} NO_2 (absorbing band due to symmetric stretching
        vibration)

1332 cm^{-1} SO_2 (absorbing band due to asymmetric stretching
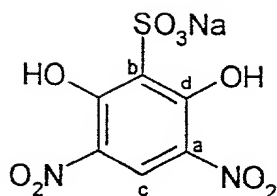   vibration)

1154 cm^{-1} SO$_2$ (absorbing band due to symmetric stretching vibration)

Example 8 (<u>Nitration step R2</u>)

4.12 g of 9.44 g of a mixture of 2-sulfonic acid-4,6-dinitroresorcin sodium salt obtained in Example 7 and sodium sulfate were added to 100 g of a mixed solution of water and ethanol in a ratio of 20:80. After the mixture was sludged and filtered under heat at 80°C, the filtrate was cooled by allowing it to stand at room temperature, so that the deposition of crystals was observed. The crystals were collected by filtration and then air-dried under nitrogen to obtain 1.18 g of yellow crystals of 2-sulfonic acid-4,6-dinitroresorcin sodium salt.

The ^{13}C-NMR spectrum of 2-sulfonic acid-4,6-dinitroresorcin sodium salt synthesized in this example showed the following absorptions, and these absorptions were ascribed to carbons a to d in the following structural formula, respectively.

δ = 119.4 ppm   a (aromatic carbon substituted by NO$_2$)

δ = 125.2 ppm   b (aromatic carbon substituted by SO$_3$H)

δ = 128.9 ppm   c (aromatic carbon to which hydrogen was bonded)

δ = 155.0 ppm   d (aromatic carbon substituted by OH)

$$\begin{array}{c} SO_3Na \\ HO \overset{b}{\longrightarrow} \overset{d}{\longleftarrow} OH \\ O_2N \overset{c}{\longrightarrow} \overset{a}{\longleftarrow} NO_2 \end{array}$$

Furthermore, according to the measurement of an infrared-absorbing spectrum, the following distinctive absorption bands were observed.

5   1588 cm^{-1} NO$_2$ (absorbing band due to asymmetric stretching vibration)

1363 cm^{-1} NO$_2$ (absorbing band due to symmetric stretching vibration)

1332 cm^{-1} SO$_2$ (absorbing band due to asymmetric stretching vibration)

10

1154 cm^{-1} SO$_2$ (absorbing band due to symmetric stretching vibration)

Elementary analysis values (%) of C$_6$H$_3$N$_2$O$_9$SNa

Element	C	H	N	S	Na
Calcd.	23.86	1.00	9.27	10.59	7.61
Found	23.68	0.99	9.24	10.80	7.89

Example 9 (Hydrolysis step R3)

15.1 g (0.05 mol) of 2-sulfonic acid-4,6-dinitroresorcin sodium salt were added to 250 g of a 20 wt% aqueous sulfuric acid solution, and the resultant solution was then heated at 100°C for 7 hours, during which the gradual deposition of crystals was observed. After the re-action mass was cooled to room temperature, it was collect-

ed by filtration to obtain 8.95 g of yellow-white crystals.
The crystals were recrystallized from 500 g of ethanol, and
then air-dried under nitrogen to obtain 7.6 g of purified
4,6-dinitroresorcin.

Example 10 (R1 to R3 in sequence)

5.5 g (0.05 mol) of resorcin were slowly added to
50 g of 30% fuming sulfuric acid, and the reaction mass was
then heated to 90°C to thereby become a dark-red solution.
The production of resorcin 2,4,6-trisulfonate was confirmed
by HPLC analysis. The sulfonated mass was cooled with ice,
and 10.5 g (0.1 mol) of 60% nitric acid was then added
dropwise thereto, so that heat was vigorously generated and
the reaction mass became a yellow-brown slurry.

The nitrated mass was added to 100 g of ice, and
then heated to 100°C to carry out hydrolysis, so that the
gradual deposition of crystals was observed. The crystals
were collected by filtration and air-dried under nitrogen
to obtain 8.02 g (yield = 80.3% based on resorcin) of 4,6-
dinitroresorcin.

Example 11 (Steps R1 to R4)

55 g (0.5 mol) of resorcin were slowly added to
500 g of 30 wt% fuming sulfuric acid, and the mixture was
heated to 90°C, so that the reaction mass became a dark-red
solution. The production of resorcin 2,4,6-trisulfonate
was confirmed by HPLC analysis.

The sulfonated mass was cooled with ice, and 105 g

(1.0 mol) of 60 wt% nitric acid was added dropwise thereto, so that heat was vigorously generated and the reaction mass became a yellow-brown slurry. This nitrated mass was added to 1,095 g of ice, and then heated to 100°C to carry out hydrolysis, so that the gradual deposition of crystals was observed. The crystals were collected by filtration, sludged with 500 g of water, and then air-dried under nitrogen to obtain 81.2 g (yield = 81.2%) of crude 4,6-dinitroresorcin.

30 g of crude 4,6-dinitroresorcin were recrystallized in 1,500 g of ethanol to obtain 24.1 g of purified 4,6-dinitroresorcin. Next, 4.0 g of this purified 4,6-dinitroresorcin were added to methanol, and 0.0396 g of 5% palladium carbon (a 50% wet product) was then added thereto, followed by hydrogenation at 60°C under an average hydrogen pressure of 0.8 MPaG. The reaction mass was poured into a 5% aqueous hydrochloric acid solution containing 6,000 ppm of stannous chloride, and then filtered to remove the catalyst. Afterward, analysis was carried out by HPLC, and it was confirmed that desired 4,6-diaminoresorcin was produced in a yield of 96.2 mol%. The solvent was removed from the filtrate by an evaporator to obtain the crystals of crude 4,6-dinitroresorcin. The crystals were dissolved in 21.3 g of water containing 0.32 g of stannous chloride, and 0.2 g of activated carbon was added to the solution. Thereafter, the solution was stirred for 30 minutes and then filtered

to remove the activated carbon. When 16.0 g of 36% hydro-
chloric acid were gradually added dropwise to the filtrate,
the gradual deposition of crystals was observed. The crys-
tals were collected by filtration and then dried at 50°C

5 under reduced pressure to obtain 3.03 g (yield = 46.4%) of
4,6-diaminoresorcin dihydrochloride.

Example 12

10 g of purified 4,6-dinitorresorcin obtained in
Example 11 were added to 73.4 g of a 5.2% aqueous hydro-

10 chloric acid solution. To the solution was added 0.9 g of
2% platinum carbon (a 56% water-containing product), and
hydrogenation was then carried out at 60°C under a hydrogen
pressure of 0.8 MPa. After the reaction mass was filtered
to remove the catalyst, 0.75 g of activated carbon was

15 added to the filtrate. Thereafter, the filtrate was stir-
red for 30 minutes and then filtered to remove the activat-
ed carbon. When 23 g of hydrogen chloride were added to
the filtrate, the gradual deposition of crystals was ob-
served. The crystals were collected by filtration and then

20 dried under reduced pressure to obtain 10.2 g (yield =
95.7%) of 4,6-diaminoresorcin dihydrochloride.

Example 13

32 g (0.16 mol) of 4,6-dinitroresorcin produced in
the same manner as in Example 10 were added to 1,440 g of

25 ethyl acetate, and the mixture was then heated to 80°C to
become a homogeneous solution. Next, 200 g of hot water at

80°C were added to the mixture, and a pH electrode was then immersed into the solution. Afterward, a 49% aqueous sodium hydroxide solution was added dropwise thereto to adjust a pH of the system to 4.3, and the solution was then stir-

5   red at the same temperature for one hour.

The stirring was terminated, and the solution was then allowed to stand for one hour. Thereafter, water was discharged through the bottom of the flask. 200 g of hot water was added to the remaining 4,6-dinitroresorcin ethyl

10 acetate solution in the flask, followed by stirring at 80°C for one hour. After the stirring was stopped, the solution was allowed to stand for one hour and the resultant liquid phases were then separated. This operation was further repeated twice.

15 The remaining 4,6-dinitroresorcin ethyl acetate solution in the flask was gradually cooled to 20°C to deposit yellow crystals. This solution was suction-filtered, washed with hot water, and then dried at 30°C, thereby obtaining 20.8 g of 4,6-dinitroresorcin.

20 20 g of the thus obtained 4,6-dinitroresorcin, 0.4 g of 2% platinum carbon and 146.7 g of a 5.2% aqueous hydrochloric acid solution were placed in a 0.3-liter autoclave made of tantalum, and hydrogenation reaction was then carried out at a reaction temperature of 60°C and a stir-

25 ring speed of 1,000 rpm under a hydrogen pressure of 0.78 MPa. The reaction was completed in a reaction time of 95

minutes. Thereafter, the catalyst was filtered out, where-
by a colorless transparent reaction solution was obtained.
The reaction results in this case were such that the con-
version rate of 4,6-dinitroresorcin was 100% and the yield
5   of 4,6-diaminoresorcin dihydrochloride was 98%.

In succession, 35 g of hydrogen chloride were
blown into the above reaction solution to deposit white
crystals. This solution was filtered, washed with acetone,
and then dried at 30°C to obtain 20.4 g of white 4,6-
10 diaminoresorcin dihydrochloride.

Example 14

32 g of 4,6-dinitroresorcin produced in the same
manner as in Example 10 were added to 128 g of methanol,
and the resulting mixture was then heated to 50°C. To the
15 obtained slurry solution was added a 49% aqueous sodium hy-
droxide solution to adjust the pH of the solution to 4.3.
After stirred at the same temperature for one hour, the so-
lution was cooled to 20°C. This treated solution was fil-
tered, washed with methanol and then water, and dried at
20 30°C to obtain 31.2 g of 4,6-dinitroresorcin.

20 g of the thus obtained 4,6-dinitroresorcin, 0.4
g of 2% platinum carbon and 146.7 g of a 5.2% aqueous hy-
drochloric acid solution were placed in a 0.3-liter auto-
clave made of tantalum, and hydrogenation reaction was then
25 carried out at a reaction temperature of 60°C and a stir-
ring speed of 1,000 rpm under a hydrogen pressure of 0.78

MPa. The reaction was completed in a reaction time of 100
minutes. Thereafter, the catalyst was filtered out to ob-
tain a reaction solution. The reaction results in this
case were such that the conversion rate of 4,6-

5   dinitroresorcin was 100% and the yield of 4,6-
diaminoresorcin dihydrochloride was 97.5%.

Example 15

50 g of 4,6-dinitroresorcin produced in the same
manner as in Example 10 were added to 570 g of water, and

10 40.8 g of a 49% aqueous sodium hydroxide solution were
added to the mixture at a temperatures of 20 to 30°C to
prepare a homogeneous solution. A 36% aqueous hydrochloric
acid solution was added dropwise to the above homogenous
solution to adjust the pH of the solution to 4.3, so that

15 the material became a slurry state. This slurry was fil-
tered, washed with water, and then dried at 30°C to obtain
49 g of 4,6-dinitroresorcin.

20 g of the thus obtained 4,6-dinitroresorcin, 0.4
g of 2% platinum carbon and 146.7 g of a 5.2% aqueous hy-

20 drochloric acid solution were placed in a 0.3-liter auto-
clave made of tantalum, and hydrogenation reaction was then
carried out at a reaction temperature of 60°C and a stir-
ring speed of 1,000 rpm under a hydrogen pressure of 0.78
MPa. The reaction was completed in a reaction time of 100

25 minutes. Thereafter, the catalyst was filtered out to ob-
tain a reaction solution. The reaction results in this

case were such that the conversion rate of 4,6-dinitroresorcin was 100% and the yield of 4,6-diaminoresorcin dihydrochloride was 97.6%.

Example 16 (Steps R1 to R4 and polymerization of
5 PBO)

110.0 g (1 mol) of resorcin were slowly added to 1,000 g of 30% fuming sulfuric acid, and the mixture was then heated up to 50°C, so that a reaction mass became a dark-red solution. According to HPLC analysis, the produc-
10 tion of resorcin 2,4,6-trisulfonate was confirmed.

The sulfonated mass was cooled with ice, and 210 g (2 mol) of 60 wt% nitric acid were added dropwise thereto, so that heat was vigorously generated and the reaction mass became a yellow-brown slurry.

15 The nitrated mass was poured into 2,200 g of ice, followed by hydrolysis at 100°C for 7 hours, so that the gradual deposition of crystals was observed. The solution was cooled to room temperature and then filtered, and the obtained crystals were washed with ethanol, filtered and
20 air-dried under nitrogen to obtain 130.5 g (yield = 65.2%) of 4,6-dinitroresorcin.

This 4,6-dinitroresorcin was placed in an auto-clave, and 660 ml of methanol and 2.7 g of 5% Pd/C were further added to the autoclave. Here, hydrogenation reac-
25 tion was carried out at 60°C under a hydrogen pressure of 0.78 MPa. When the absorption of hydrogen was no longer

observed, the reaction mass was cooled to room temperature, and then poured into 760 g of a 5% aqueous hydrochloric acid solution to dissolve the product therein. After the mixture was filtered to remove the catalyst, the solvent

5   was removed therefrom by an evaporator to obtain 133.6 g (yield = 62.7%) of crude 4,6-diaminoresorcin dihydrochloride.

     This crude 4,6-diaminoresorcin dihydrochloride was dissolved in 670 g of water containing 10 g of stannous

10   chloride, and 11 g of activated carbon were added for a discoloration treatment. The mixture was filtered to remove the activated carbon, and 510 g of 36% hydrochloric acid were added dropwise to the filtrate to deposit crystals, which were then filtered out to obtain 106.6 g (yield

15   = 50.01%) of purified 4,6-diaminoresorcin dihydrochloride.

     40% by weight of 85% H_3PO_4 and 60 wt% of 115% polyphosphoric acid were mixed with each other to prepare a polyphosphoric acid solution (a PPA solution) containing 74.9% of P_2O_5. Then, 22.82 g (0.11 mol) of the above-

20   described purified 4,6-diaminoresorcin dihydrochloride were added to 88.6 g of the PPA solution, and the solution was stirred and then heated at 50 to 80°C for about 20 hours under reduced pressure to remove hydrochloric acid therefrom. To this mixture were added 17.96 g (0.11 mol) of

25   terephthalic acid, and then 61.2 g of P_2O_5 were added thereto to adjust the content of P_2O_5 in the mixture to

87.2 wt%. This mixture was stirred at 100°C for 15 hours under argon stream. Then, while the mixed solution was vigorously stirred, its temperature was elevated up to 178°C within 40 minutes, and at this temperature, the solu-

5 tion was further stirred for 25 hours. Next, the temperature of the solution was elevated up to 185°C within one hour, and at this temperature, the solution was allowed to react for 25 hours to obtain a reaction solution containing poly(p-phenylenebenzobisoxazole) (PBO). This reaction so-

10 lution was precipitated in water, and fully washed with water to prepare a PBO powder from which the PPA was completely removed. The intrinsic viscosity of the obtained PBO was 25.2 dl/g (30°C, methanesulfonic acid).